(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 1 262 312 A2

(12) EUROPEAN PATENT APPLICATION

(43) Date of publication:
04.12.2002 Bulletin 2002/49

(51) Int Cl.^{7}: **B32B 27/08**, B32B 27/34

(21) Application number: 02011820.4

(22) Date of filing: 28.05.2002

(84) Designated Contracting States:
AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU MC NL PT SE TR
Designated Extension States:
AL LT LV MK RO SI

(30) Priority: 31.05.2001 IT MI20011151

(71) Applicant: Ausimont S.p.A.
20121 Milano (IT)

(72) Inventors:
- Abusleme,Julio A.
21047 Saronno, Varese (IT)
- Manzoni, Claudia
40100 Bologna (IT)
- Besana, Gaimbattista
22066 Mariano Comense, Como (IT)

(74) Representative: Sama, Daniele, Dr. et al
Sama Patents
Via Morgagni, 2
20129 Milano (IT)

(54) Multilayers of polyamides and CPVC

(57) A multilayer comprising at least one layer A) of at least one thermoprocessable polymer containing at least 5% by weight of chlorinated polyvinyl chloride (CPVC) and one layer B) based on polyamides having an amount of $-NH_2$ end groups in the range 20-300 μeq/g.

EP 1 262 312 A2

Description

[0001] The present invention relates to multilayers (laminates) comprising at least one polymer layer containing at least 5% of chlorinated polyvinyl chloride (CPVC) and one polyamide layer, characterized in having a complete adhesion among the layers. The adhesion between the layers is so high that at the delamination tests the specimen breaks without the layer separation.

[0002] Said multilayers show, besides a high adhesion among the layers, good mechanical properties, good chemical and flame resistance.

[0003] It is known that polyamides have good mechanical properties but a poor resistance to flame and to chemical agents. CPVC shows a poor ductility but has a good resistance to flame and to chemical agents.

[0004] The need was therefore felt to have available laminates showing the good mechanical properties of the polyamides combined with the good resistance to flame and to chemical agents of CPVC.

[0005] CPVC contains from 58% to 75% by weight of chlorine and is obtained by PVC chlorination.

[0006] The polyvinylchloride (PVC) has a chlorine content of 56.8% by weight.

[0007] Tests carried out by the Applicant have shown that by a bilayer of CPVC polymers with polyamides, obtained for example by applying a pressure on the overlapped polymer layers maintained at the softening temperature or by co-extruding the layers, the adhesion is not obtained.

[0008] The Applicant has surprisingly and unexpectedly found that it is possible to obtain multilayers, having a complete adhesion between CPVC and polyamides when polyamides are characterized by having an amount of $-NH_2$ end groups of at least 20 μeq/g.

[0009] An object of the present invention is therefore a multilayer comprising at least one bilayer (laminate) between:

A) a layer of at least one thermoprocessable polymer containing at least 5% by weight of chlorinated polyvinyl chloride (CPVC) having a chlorine content from 58% to 75% by weight, preferably from 60% to 70% by weight;

B) a layer based on polyamides having an amount of $-NH_2$ end groups in the range 20-300 μeq/g, preferably 30-150 μeq/g.

[0010] The thermoprocessable polymer of layer A) can be selected from PVC and/or polyvinylidene chloride (PVDC). Preferably layer A) is formed by CPVC.

[0011] Optionally layer B) of the bilayer A/B can be placed on top of another layer A) or on top of layer C) based on thermoprocessable copolymers of ethylene with chlorotrifluoroethylene (CTFE), and/or tetrafluoroethylene (TFE), preferably CTFE, and with acrylic monomers of formula:

$$CH_2=CH-CO-O-R_2 \qquad (a)$$

wherein R_2 is H or a linear or branched C_1-C_{20} alkyl radical, cycloalkyl radical; R_2 optionally contains Cl, O, N and/or one or more functional groups selected from -OH, -COOH, epoxide, ester or ether; wherein the monomer (a) amount is in the range 0.01-15% by moles with respect to the sum of the monomers of ethylene and of CTFE and/or TFE.

[0012] The thermoprocessable copolymers of layer C) are preferably formed by:

- from 10% to 70% by moles, preferably from 35% to 55% of ethylene;
- from 30% to 90% by moles, preferably from 45% to 65%, of a fluorinated monomer selected from tetrafluoroethylene, chlorotrifluoroethylene, or mixtures thereof;
- from 0.05% to 15% by moles of the acrylic co-monomer (a) referred to the sum of the previous monomers.

[0013] As acrylic monomer of formula (a), n-butylacrylate (n-BuA) is preferably used.

[0014] The layer C) can also be formed by a blend of the copolymers of layer C) and the thermoprocessable copolymers of ethylene with chlorotrifluoroethylene (CTFE) and/or tetrafluoroethylene (TFE), provided that the blend contains an amount of acrylic monomer (a) in the range 0.01%-15% by moles with respect to the total sum of the monomers of ethylene and of CTFE and/or TFE of the blend.

[0015] Preferably in layer C) the monomer amount of (a) is lower than 1% by moles with respect to the sum of the monomers of ethylene and chlorotrifluoroethylene and/or tetrafluoroethylene.

[0016] Optionally on top of layer C) of the multilayer A/B/C, can be put a layer C1) formed by thermoprocessable copolymers of ethylene with chlorotrifluoroethylene (CTFE) and/or tetrafluoroethylene (TFE).

[0017] On top of layer A) of the bilayer A/B another layer B) can be put, which can be further in contact with a layer C) and subsequently on layer C) can be placed a layer C1). Examples of possible multilayers are:

- A/B/A
- A/B/C
- A/B/C/C1
- B/A/B
- C/B/A/B
- C1/C/B/A/B
- C/B/A/B/C
- C1/C/B/A/B/C
- C1/C/B/A/B/C/C1

[0018] In a multilayer that ends with layer B, optional-

ly, on this layer can be placed a layer B1) formed by a polyamide with a content of $-NH_2$ end groups lower than 20 μeq/g.

[0019] The polyamides having an amount of $-NH_2$ end groups, higher than 20 μeq/g, can be prepared according to known methods, for example according. to USP 4,543,378, wherein a chain transfer agent is used in the polymerization phase. As example of chain transfer agents, m- or p-xylylen-diamine, hexamethylendiamine or dodecamethylendiamine can be cited.

[0020] The polyamide of layer B) having an amount of end groups $-NH_2$ higher than 20 μeq/g can also be obtained by mixing polyamides having different contents of $-NH_2$ end groups so that the final mixture contains an amount of $-NH_2$ end groups higher than 20 μeq/g.

[0021] The polyamides of layer B), can be a (co)polyamide, for example, polyamide 6 (PA 6), polyamide 66 (PA 66), polyamide 11 (PA 11), polyamide 12 (PA 12).

[0022] The polyamides of layer B), can optionally contain diamines.

[0023] The Applicant has also found that the multilayers of the present invention endowed with excellent adhesions can be obtained by using as layer B) a blend of a polyamide having an amount of $-NH_2$ end groups lower than 20 μeq/g and 0.1-5% by weight, preferably 0.5-2% by weight, of one or more diamines.

[0024] The polyamides having $-NH_2$ end groups lower than 20 μ-eq/g, can be (co)polyamides, such as for example. polyamide 6, polyamide 66, polyamide 11, polyamide 12.

[0025] Non limitative examples of diamines are protected amines, such as for example hexamethylendiaminecarbamate and N,N'-dicinnamylidene-1,6 hexanediamine, C_4-C_{20} aliphatic diamines, such as for example dodecyldiamine and decyldiamine, aromatic diamines. such as for example para-xylilendiamine. Aliphatic and aromatic protected diamines are preferred.

[0026] The single layers of the invention can optionally contain additives such as fillers for example polytetrafluoroethylene (PTFE), silicates, graphite, titanium dioxide, lubrificants, pigments, fire retardants, plasticizers, thermal and UV stabilizers.

[0027] The multilayer structures of the present invention can be obtained by co-extrusion. Alternatively, the single layers are laminated by compression at the softening temperature.

[0028] When layer A) and layer C) are formed by self-supporting plaques suitable to build, by their combination, hybrid structures such as for example those used in wet-benches, their junction-coupling can be carried out by welding along a contact line using a weld rod, constituted by the above defined polyamide of layer B).

[0029] Optionally on top of layers A) and C) a layer B) can be placed.

[0030] The multilayers according to the present invention can be used as structural elements for benches, coating panels, in the building of structures such as, for example, the wet-benches used in the semiconductor industry.

[0031] Some illustrative examples follow, which are not limitative of the present invention.

[0032] The following characterizations were carried out on the polymers of the examples:

- Melt Flow Index (M.I.)
  The M.I. of the fluorinated polymers is measured according to the method ASTM 3275-89, at 275°C and with a load of 2.16 kg;
- Second melting temperature (T_{mII})
  The T_{mII} of the fluorinated polymers is determined by differential scanning calorimetry (DSC);
- Glass transition temperature (Tg)
  The Tg of the polymers CPVC is determined by differential scanning calorimetry (DSC);
- Chlorine content in CPVC
  it has been determined by elemental analysis;
- $-NH_2$ End groups
  The number of the end groups $-NH_2$ of polyamides is determined by preparing a solution at 2% of polyamide in m-cresol and subsequent titration with perchloric acid.

EXAMPLES

EXAMPLE 1

Layer A)

CPVC

[0033] From a CPVC polymer having a Tg of 112°C and a chlorine content of 64.24% by weight, plaques having a thickness of 1.5 mm have been obtained by compression moulding.

Layer B)

Polyamide 12 (PA 12) having $-NH_2$ end groups equal to 110 μeq/g

[0034] Some plaques of the polyamide having a thickness of 1.5 mm have been obtained by compression moulding.

Preparation of the A/B laminate

[0035] The plaques of the single layers A and B, previously obtained, have been overlapped and kept under pressure at a temperature of 240°C for 5 minutes.

[0036] By applying a mechanical force one tries to separate layer A from layer B.

[0037] One cannot measure the adhesion force between layer A and layer B. By increasing the force to separate the layers, one breaks the manufactured arti-

cle without obtaining the delamination. This shows that the laminate according to the invention shows a high adhesion.

EXAMPLE 2 (comparative)

Layer A)

[0038] The same polymer of Example 1 is used.

Layer B)

PA 12 having $-NH_2$ end groups equal to 13 μeq/g

[0039] Some plaques of the polyamide having a thickness of 1.5 mm have been obtained by compression moulding.

Preparation of the A/B laminate

[0040] The plaques of the single layers A and B, previously obtained, have been overlapped and kept under pressure at a temperature of 240°C for 5 minutes.

[0041] The A/B laminate does not show any adhesion between the layers.

EXAMPLE 3 (comparative)

Layer A)

[0042] The same polymer of Example 1 is used.

Layer B)

PA 12 having $-NH_2$ end groups equal to 18 μeq/g

[0043] The polyamide has been obtained by mechanically mixing 50 g of PA 12 of Example 1 ($-NH_2$ = 110 μeq/g) with 950 g of PA 12 of Example 2 ($-NH_2$ = 13 μeq/g). Then the blend has been pelletized in a single screw Brabender extruder in Hastelloy C-276 having a diameter of 18 mm and a length equivalent to 25 times the diameter, with a melt temperature of 225°C. Plaques having a thickness of 1.5 mm have been prepared from the granules by compression moulding.

Preparation of the A/B laminate

[0044] The plaques of the single layers A and B, previously obtained, have been overlapped and kept under pressure at a temperature of 240°C for 5 minutes.

[0045] The A/B laminate does not show any adhesion between the layers.

EXAMPLE 4

Layer A)

[0046] The same polymer of Example 1 is used.

Layer B)

PA 12 having $-NH_2$ end groups equal to 23 μeq/g

[0047] The polyamide has been obtained by mechanically mixing 100 g of PA 12 of Example 1 ($-NH_2$ = 110 μeq/g) with 900 g of PA 12 of Example 2 ($-NH_2$ = 13 μeq/g). Then the blend has been pelletized in a single screw Brabender extruder in Hastelloy C-276 having a diameter of 18 mm and a length equivalent to 25 times the diameter, with a melt temperature of 225°C. Plaques having a thickness of 1.5 mm have been prepared from the granules by compression moulding.

Preparation of the A/B laminate

[0048] The plaques of the single layers A and B, previously obtained, have been overlapped and kept under pressure at a temperature of 240°C for 5 minutes.

[0049] By applying a mechanical force one tries to separate layer A from layer B.

[0050] One cannot measure the adhesion force between layer A and layer B. By increasing the force to separate the layers, one breaks the manufactured article without obtaining the delamination. This shows that the laminate according to the invention shows a high adhesion.

EXAMPLE 5

Layer A)

[0051] The same polymer of Example 1 is used.

Layer B)

PA 12 having $-NH_2$ end groups equal to 32 μeq/g

[0052] The polyamide has been obtained by mechanically mixing 200 g of PA 12 of Example 1 ($-NH_2$ = 110 μeq/g) with 800 g of PA 12 of Example 2 ($-NH_2$ = 13 μeq/g). Then the blend has been pelletized in a single screw Brabender extruder in Hastelloy C-276 having a diameter of 18 mm and a length equivalent to 25 times the diameter, with a melt temperature of 225°C. Plaques having a thickness of 1.5 mm have been prepared from the granules by compression moulding.

Preparation of the A/B laminate

[0053] The plaques of the single layers A and B, previously obtained, have been overlapped and kept under

pressure at a temperature of 240°C for 5 minutes.

[0054] By applying a mechanical force one tries to separate layer A from layer B.

[0055] One cannot measure the adhesion force between layer A and layer B. By increasing the force to separate the layers, one breaks the manufactured article without obtaining the delamination. This shows that the laminate according to the invention shows a high adhesion.

EXAMPLE 6

Layer A)

[0056] The same polymer of Example 1 is used.

Layer B)

PA 12 having -NH_2 end groups equal to 45 μeq/g

[0057] The polyamide has been obtained by mechanically mixing 330 g of PA 12 of Example 1 (-NH_2 = 110 μeq/g) with 670 g of PA 12 of Example 2 (-NH_2 = 13 μeq/g). Then the blend has been pelletized in a single screw Brabender extruder in Hastelloy C-276 having a diameter of 18 mm and a length equivalent to 25 times the diameter, with a melt temperature of 225°C. Plaques having a thickness of 1.5 mm have been prepared from the granules by compression moulding.

Preparation of the A/B laminate

[0058] The plaques of the single layers A and B, previously obtained, have been overlapped and kept under pressure at a temperature of 240°C for 5 minutes.

[0059] By applying a mechanical force one tries to separate layer A from layer B.

[0060] One cannot measure the adhesion force between layer A and layer B. By increasing the force to separate the layers, one breaks the manufactured article without obtaining the delamination. This shows that the laminate according to the invention shows a high adhesion.

EXAMPLE 7

Layer A)

[0061] The same polymer of Example 1 is used.

Layer B)

Polyamide PA 12 having -NH_2 end groups equal to 13 μeq/g blended with 1% by weight of diamine

[0062] One kilogram of polyamide (PA 12) in granules, having -NH_2 end groups equal to 13 μeq/g, has been blended with 1% by weight of hexamethylendiamine monocarbamate. Then it has been pelletized in a single screw Brabender extruder in Hastelloy C-276 having a diameter of 18 mm and a length equivalent to 25 times the diameter, with a melt temperature of 225°C. Plaques having a thickness of 1.5 mm have been prepared from the granules by compression moulding.

Preparation of the A/B laminate

[0063] The plaques of the single layers A and B, previously obtained, have been overlapped and kept under pressure at a temperature of 240°C for 5 minutes.

[0064] By applying a mechanical force one tries to separate layer A from layer B.

[0065] One cannot measure the adhesion force between layer A and layer B. By increasing the force to separate the layers, one breaks the manufactured article without obtaining the delamination. This shows that the laminate according to the invention shows a high adhesion.

EXAMPLE 8

Layer A)

[0066] The polymer of Example 1 is used.

Layer B)

[0067] The polyamide of Example 1 is used.

Layer C)

E/CTFE/n-BuA 40/55/5% by moles

[0068] The copolymer has been prepared by known methods described for example in EP 866 079 and is characterized by:

- M.I. 15 g/10'
- T_{mII} 180°-200°C.

[0069] Plaques having a thickness of 1.5 mm have been obtained from the copolymer by compression moulding.

Preparation of the A/B/C multilayer

[0070] The plaques of the single layers A, B and C, previously obtained, have been overlapped in the order A/B/C, and kept under pressure at a temperature of 240°C for 5 minutes.

[0071] By applying a mechanical force one tries to separate layer A from layer C of the multilayer A/B/C.

[0072] One cannot measure the separation force. This shows that the multilayer of the invention shows a high adhesion among the layers.

EXAMPLE 9

Layer A)

[0073] The same polymer of Example 1 is used.

Layer B)

[0074] The same polyamide of Example 6 is used.

Layer C)

[0075] The same copolymer of Example 8 is used.

Preparation of the A/B/C multilayer

[0076] The plaques of the single layers A, B and C, previously obtained, have been overlapped in the order A/B/C, and kept under pressure at a temperature of 240°C for 5 minutes.

[0077] By applying a mechanical force one tries to separate layer A from layer C of the A/B/C multilayer.

[0078] One cannot measure the separation force. This shows that the multilayer of the invention shows a high adhesion among the layers.

EXAMPLE 10

Layer A)

[0079] The same polymer of Example 1 is used.

Layer B)

[0080] The same polyamide of Example 7 is used.

Layer C)

[0081] The same copolymer of Example 8 is used.

Preparation of the A/B/C multilayer

[0082] The plaques of the single layers A, B and C, previously obtained, have been overlapped in the order A/B/C, and kept under pressure at a temperature of 240°C for 5 minutes.

[0083] By applying a mechanical force one tries to separate layer A from layer C of the A/B/C multilayer.

[0084] One cannot measure the separation force. This shows that the multilayer of the invention shows a high adhesion among the layers.

EXAMPLE 11 (comparative)

Layer A)

[0085] The same polymer of Example 1 is used.

Layer C)

[0086] The same copolymer of Example 8 is used.

Preparation of the A/C laminate

[0087] The plaques of the single layers A and C, previously obtained, have been overlapped and kept under pressure at a temperature of 240°C for 5 minutes.

[0088] The laminate A/C does not show any adhesion between the layers.

Claims

1. A multilayer comprising at least one bilayer (laminate) between:

   A) a layer of at least one thermoprocessable polymer containing at least 5% by weight of chlorinated polyvinyl chloride (CPVC) having a chlorine content from 58% to 75% by weight, preferably from 60% to 70% by weight;
   B) a layer based on polyamides having an amount of $-NH_2$ end groups in the range 20-300 μeq/g, preferably 30-150 μeq/g.

2. A multilayer (laminate) according to claim 1, wherein layer B) of the A/B bilayer is placed on top of layer A) or of layer C) based on thermoprocessable copolymers of ethylene with chlorotrifluoroetylene (CTFE) and/or tetrafluoroethylene (TFE), preferably CTFE, and with acrylic monomers of formula:

$$CH_2=CH\text{-}CO\text{-}O\text{-}R_2 \qquad (a)$$

   wherein:

   R_2 is H or a linear or branched, C_1-C_{20} alkyl radical, cycloalkil radical; R_2 optionally contains Cl, O, N and/or one or more functional groups selected from -OH, -COOH, epoxide, ester or ether; wherein the monomer (a) amount is in the range 0.01-15% by moles with respect to the sum of the monomers of ethylene and of CTFE and/or TFE.

3. A multilayer according to claims 1-2, wherein the thermoprocessable copolymer of layer A) is formed by polyvinyl chloride (PVC) and/or polyvinylidene chloride (PVDC).

4. A multilayer according to claims 2-3, wherein the thermoprocessable copolymers of layer C) are formed by:

- from 10% to 70% by moles, preferably from 35% to 55% of ethylene;
- from 30% to 90% by moles, preferably from 45% to 65%, of a fluorinated monomer selected from tetrafluoroethylene, chlorotrifluoroethylene, or mixtures thereof;
- from 0.05% to 15% by moles of the acrylic comonomer

(a) referred to the sum of the previous monomers.

5. A multilayer according to claims 2, 3, 4, wherein n-butylacrylate (n-BuA) is used as acrylic monomer of formula (a).

6. A multilayer according to claims 2-5, wherein layer C) is formed by a blend of the copolymers of layer C) and the thermoprocessable copolymers of ethylene with chlorotrifluoroethylene (CTFE) and/or tetrafluoroethylene (TFE), provided that the blend contains an amount of acrylic monomer (a) in the range 0.01%-15% by moles with respect to the total sum of the monomers of ethylene and of CTFE and/or TFE of the blend.

7. A multilayer according to claims 2-6, wherein on top of layer C) of the multilayer A/B/C there is a layer C1) formed by thermoprocessable copolymers of ethylene with chlorotrifluoroethylene (CTFE) and/ ortetrafluoroethylene (TFE).

8. A multilayer according to claims 1-7, wherein on top of layer A) of the bilayer A/B there is a layer B); on the latter layer there is optionally in sequence a layer C) and a layer C1).

9. A multilayer according to claims 1-8, wherein when the multilayer ends with layer B), on this layer there is a layer B1) formed by a polyamide with a content of $-NH_2$ end groups lower than 20 μeq/g.

10. A multilayer according to claims 1-9, wherein the polyamide of layer B) having an amount of $-NH_2$ end groups higher than 20 μeq/g is obtained by mixing polyamides having different contents of $-NH_2$ end groups so that the final mixture contains an amount of $-NH_2$ end groups higher than 20 μeq/g.

11. A multilayer according to claims 1-10, wherein layer B) is a blend of a polyamide having an amount of $-NH_2$ end groups lower than 20 μeq/g and 0.1-5% by weight, preferably 0.5-2% by weight, of one or more diamines.

12. A multilayer according to claim 11, wherein the diamines are selected from the group formed by: hexamethylendiaminecarbamate, N,N'-dicinnamylidene-1,6 hexandiamine, C_4-C_{20} aliphatic diamines, such as dodecyldiamine and decyldiamine, aromatic diamines, such as para-xylilendiamine.

13. Structures as wet-benches obtained by welding the multilayer according to claims 1-12, wherein a welding layer of polyamide B) interposed and/or in contact with the surfaces A) and C) to be put together, is used.

(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 1 262 312 A3

(12) **EUROPEAN PATENT APPLICATION**

(88) Date of publication A3:
05.02.2003 Bulletin 2003/06

(51) Int Cl.7: **B32B 27/08**, B32B 27/34, B32B 27/30

(43) Date of publication A2:
04.12.2002 Bulletin 2002/49

(21) Application number: **02011820.4**

(22) Date of filing: **28.05.2002**

(84) Designated Contracting States:
AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU MC NL PT SE TR
Designated Extension States:
AL LT LV MK RO SI

(30) Priority: **31.05.2001 IT MI20011151**

(71) Applicant: **Ausimont S.p.A.**
20121 Milano (IT)

(72) Inventors:
- **Abusleme,Julio A.**
  21047 Saronno, Varese (IT)
- **Manzoni, Claudia**
  40100 Bologna (IT)
- **Besana, Gaimbattista**
  22066 Mariano Comense, Como (IT)

(74) Representative: **Sama, Daniele, Dr. et al**
Sama Patents
Via Morgagni, 2
20129 Milano (IT)

(54) **Multilayers of polyamides and CPVC**

(57) A multilayer comprising at least one layer A) of at least one thermoprocessable polymer containing at least 5% by weight of chlorinated polyvinyl chloride (CPVC) and one layer B) based on polyamides having an amount of $-NH_2$ end groups in the range 20-300 μeq/g.

EP 1 262 312 A3

Printed by Jouve, 75001 PARIS (FR)

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 02 01 1820

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
A	EP 1 101 994 A (TOKAI RUBBER IND LTD) 23 May 2001 (2001-05-23) * claims 1,2,6,7 * * page 2, line 42 - line 44 * * page 3, line 31 - line 47 * * page 4, line 25 - page 5, line 57 * ---	1-13	B32B27/08 B32B27/34 B32B27/30
A	DATABASE WPI Section Ch, Week 199413 Derwent Publications Ltd., London, GB; Class A14, AN 1994-106394 XP002222192 & JP 06 055703 A (MITSUBISHI PLASTICS IND LTD), 1 March 1994 (1994-03-01) * abstract * ---	1-13	
A	EP 1 038 914 A (AUSIMONT SPA) 27 September 2000 (2000-09-27) * claims 1,13-16 * * page 2, line 41 - line 53 * * page 3, line 36 - line 45 * ---	1-13	TECHNICAL FIELDS SEARCHED (Int.Cl.7)
A	US 4 183 777 A (KLINER GEORGE J ET AL) 15 January 1980 (1980-01-15) * claim 1 * * column 1, line 26 - line 34 * * column 3, line 43 - line 47 * * column 6, line 41 - line 48 * * example 4; table 8 * -----	1-13	B32B

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	22 November 2002	Girard, S

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

EPC FORM 1503 03 82 (P04C01)

ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 02 01 1820

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

22-11-2002

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 1101994 A	23-05-2001	JP 2001208249 A	03-08-2001
		EP 1101994 A2	23-05-2001
JP 6055703 A	01-03-1994	NONE	
EP 1038914 A	27-09-2000	IT MI990549 A1	19-09-2000
		EP 1038914 A1	27-09-2000
		JP 2000313784 A	14-11-2000
		NO 20001384 A	20-09-2000
		US 6476150 B1	05-11-2002
US 4183777 A	15-01-1980	US 4100325 A	11-07-1978
		AU 512631 B2	23-10-1980
		AU 3070177 A	24-05-1979
		CA 1107928 A1	01-09-1981
		MX 147814 A	18-01-1983
		NZ 185676 A	25-10-1979
		SE 7713939 A	14-06-1978

EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82